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WEATHERING OF A METAL ARTIFACT IN A SAHARAN ENVIRONMENT:
EVIDENCE FOR A NOVEL FORM OF DESERT VARNISH

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AND JOHN F. MCCAULEY

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Weathering of a Metal Artifact in a Saharan Environment: Evidence for a Novel Form of Desert Varnish

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A dark-brown coating on the exterior of a World War II metal fuel can recovered in southwestern Egypt may be a variation of the desert varnish that develops on rock surfaces in arid regions. This suggestion is supported by results of infrared spectroscopic work, x-ray diffraction, scanning electron microscopic studies, and x-ray fluorescence. Exterior portions of the can resemble heavily varnished rock, differing completely in appearance and texture from rusty areas which had developed on portions of the interior surface. The coating consists principally of microscopic mineral deposits, some of which appear to be largely Fe-oxides and Fe-oxy-hydroxides. However many deposits are assemblages of Fe-oxides, clay minerals, and other elements typically occurring in forms of desert varnish often observed on the undersides of desert pavement stones in contact with the soil. Associated with the mineral matter is an organic component apparently deriving from residues of an original paint layer which had been removed by wind/sand scouring.

Index Headings: Desert varnish; Weathering of metal; World War II artifact; Infrared; X-ray diffraction; X-ray fluorescence.

INTRODUCTION

"The desert is now dead again, and sand blows over our old tracks, tinkling against our rusting petrol tins."—R. A. Bagnold, 1945.

"Desert varnish" is a term commonly used in reference to a natural coating which often forms on rock surfaces in arid regions worldwide. Varnish coatings consist largely of clay minerals, oxides and hydroxides of Mn and/or Fe, plus minor amounts of organic matter and other materials derived from air-borne dust and other sources external to the substrate. Rock varnish includes black, brown, and orange varieties; the color is generally indicative of the relative amounts of Fe- and Mn-oxides present. Black and brown Mn-rich forms are the more conspicuous; however, orange Fe-rich coatings containing little or no Mn often form on the underside of rocks in contact with the soil. Although the field occurrence and chemistry of desert varnish have been studied for over a century, the mechanism and rates of its formation appear complex and incompletely understood and are still the subject of debate. Most observers consider rock varnish formation in arid climates to be an extremely slow process, requiring several thousand years for full development. Nevertheless Scheffer *et al.*¹ have noted revarnishing of rocks disturbed by military maneuvers in the Sahara during World War II. Desert varnish has been considered important for its possible application to relative age dating in archeology and geomorphology. A

review of work on rock desert varnish is found in Dorn and Oberlander.^{2,3}

Despite an extensive literature concerning desert varnish, reports of its formation on other than rock surfaces appear to be lacking. This paper describes studies of a British metal fuel can found partially buried in sand sheet deposits (Fig. 1) in southwestern Egypt. The exposed exterior of the can had acquired a smooth brown coating resembling the varnished surfaces of certain rock



FIG. 1. Metal fuel can abandoned in Western Desert of Egypt between 1940 and 1942. Bottom: can in place, partly buried in sand sheet. Can was found at approximately lat. 23°N, long. 26°E. Top: same can retrieved from desert; light-colored portion was buried and retains original tan paint; thin line of rust marks edge of buried portion at sand surface. Dark portion is covered with desert varnish-like patina.

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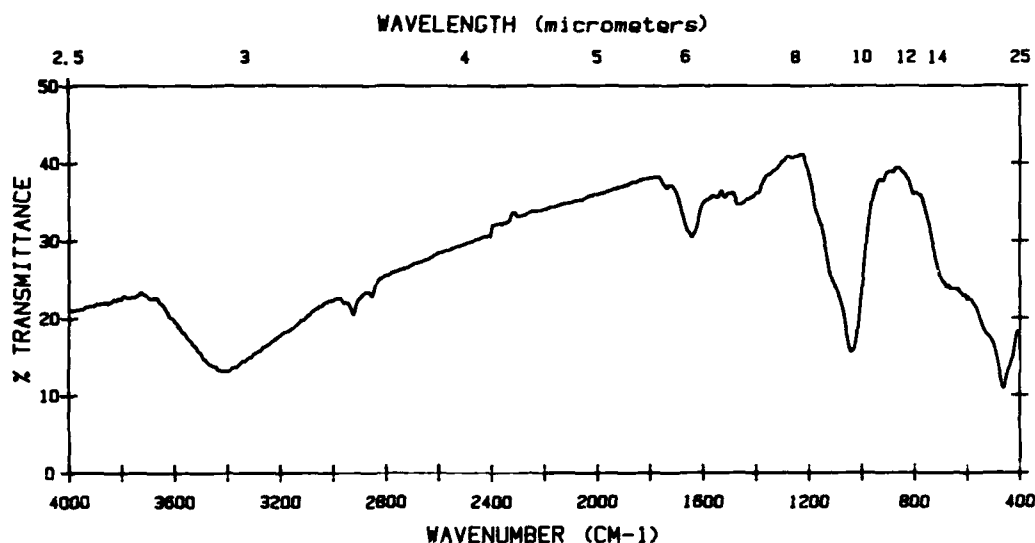


FIG. 2. Infrared spectrum of metal coating material scraped from surface. A 2.8-mg portion of powdered sample was dispersed in a 200-mg KBr pellet, 13 mm in diameter.

specimens collected previously in Death Valley, California (J. W. Eastes, unpublished work). Buried portions of the can retained the original tan exterior paint. It is believed to be one of many left in the area during military operations early in World War II.^{4,5}

EXPERIMENTAL

An infrared spectrum of coating material scraped from the metal surface is shown in Fig. 2. Absorption due to clay minerals produces spectral features at 1027, 467, and 536 cm^{-1} . Quartz absorption appears weakly at 799 cm^{-1} . Features not due to these minerals are attributable to water (3400 and 1654 cm^{-1}) and organic matter (C-H stretch doublet between 2800 and 3000 cm^{-1}).

X-ray diffraction (XRD) features (Fig. 3) of dithionite-extracted coating material oriented by sedimentation from water suspension indicate the presence of feldspar

(3.2 Å), quartz (3.3 Å), and a mixture of illite (10 Å), kaolinite (7.3 Å), and a smectitic component (12.4 Å).

Examination of the coating with an optical microscope revealed a nonhomogeneous layer consisting of reddish-brown deposits interspersed with areas much darker in color. Scanning electron microscopy (SEM) imagery (Fig. 4) shows the surface imaged with backscattered electrons which depict compositionally different areas as different shades of density. The dark tones in Fig. 4, which comprise approximately 43% of the surface area, correspond to regions rich in clay minerals, whereas the bright tones represent areas rich in Fe-materials. An edge-on view (Fig. 5) of the can wall shows the coating (upper right) to be 5 to 15 μm thick, with a distinct coating/metal interface. (The bright, thin, irregular layer at the lower left of the central metal section is tin plating on the inner surface of the can.)

Major-element composition of the dark clay-rich and bright Fe-rich areas depicted in Fig. 4 were determined by energy dispersive x-ray fluorescence (EDXRF) analysis. CHN analysis and volatiles lost on ignition (1000°C) were performed separately. These results are presented in Table I.

RESULTS AND DISCUSSION

Oxide compositions of the clay-rich and Fe-rich zones of the metal coating differ greatly, particularly for the Fe-phase (Table I). The appearance of the coating under the optical microscope suggested that the Fe-rich zones probably consist largely of iron-rust deposits and make up the reddish-brown areas mentioned above. Only relatively small concentrations of clay minerals are found in these areas. However, compositional data for the dark clay-rich zones are similar to those reported by Potter and Rossman⁶ for orange rock varnishes from the Salt Spring and Stoddard Wells localities in the Mojave Desert of California. Their data are included in the last two columns of Table I for comparison. (Potter and Rossman⁶ also reported concentrations of TiO_2 , P_2O_5 , and BaO for

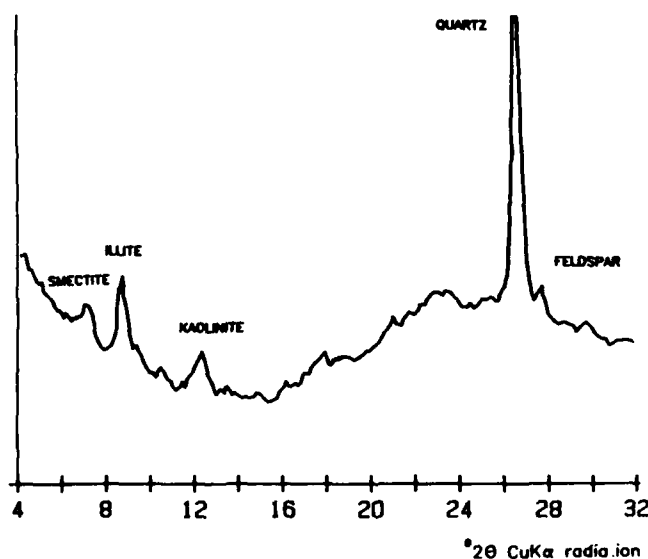


FIG. 3. X-ray diffraction features of particulate coating material.

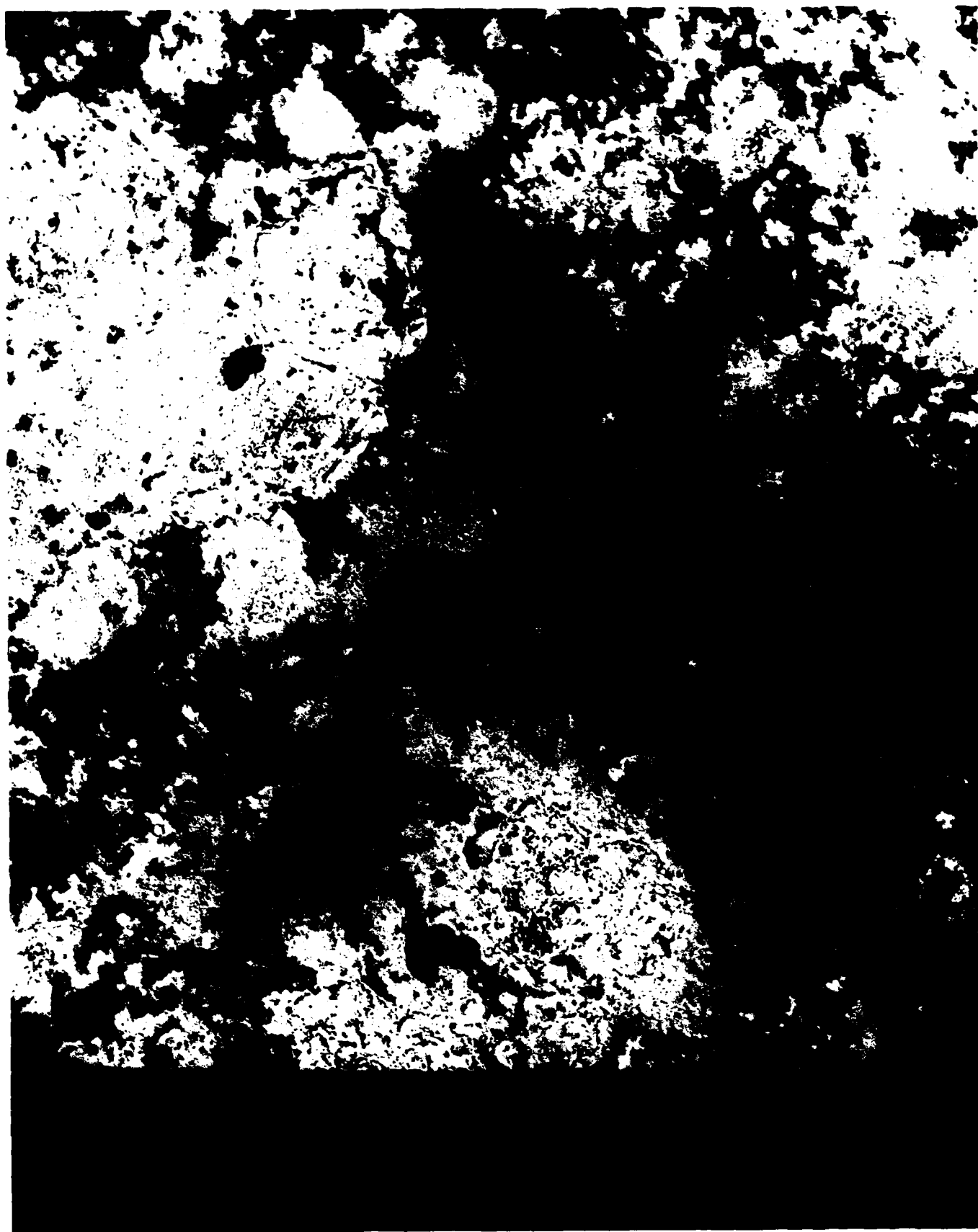


FIG. 4. Scanning electron micrograph imaged with backscattered electrons depicting compositionally different areas as different densities. Darker areas represent a clay-rich composition resembling certain varieties of rock varnish.

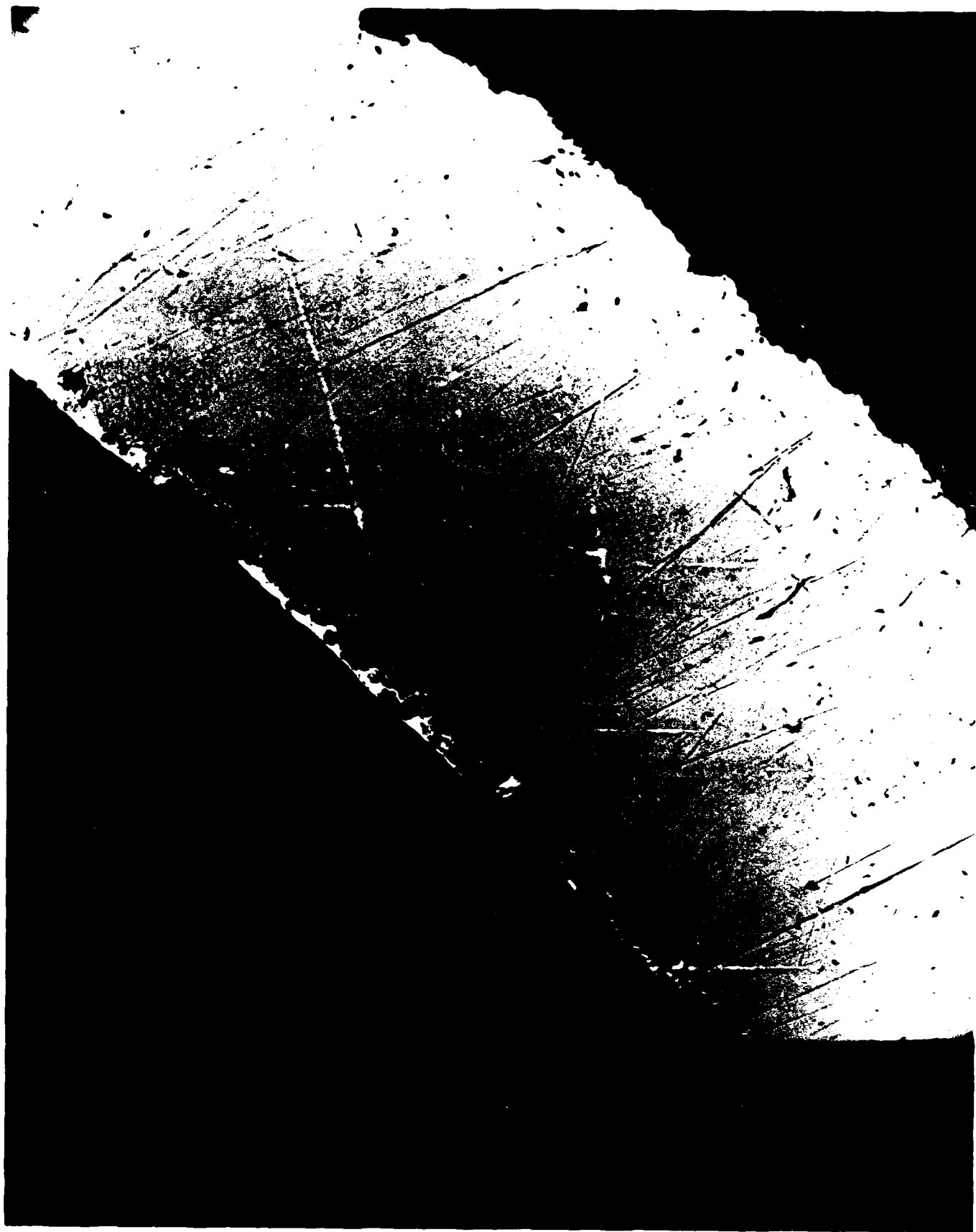


FIG. 5. Transverse section of container wall showing exterior varnish-like coating (upper right) and remnants of interior tin plating (lower left).

the orange rock varnishes. These were not found in the metal coating.)

Rock varnishes appear to be best developed on porous rocks, which apparently provide a suitable surface for the accretion of wind- or water-borne materials. Potter and Rossman conclude⁷ that clays may not be merely a passive contaminant in desert varnish but may serve as an active agent in its formation. Their model assumes a mutual dependence of the clay and metal oxide phases, in which clays depend on the oxides for resistance to erosion and the oxides depend on the clays for capillary transport and deposition. In the case of a metal substrate, initial irregular formation of microscopic rust deposits could reasonably be expected to form porous and tenacious sites for further coating development. Such a process could account for the observed patchwork pattern of Fe-rich and clay-rich areas. Thus an analog of rock desert varnish might be expected to form on any surface on which Fe- and/or Mn-oxides can be brought together with clays in a stable combination.

The metal coating was almost devoid of Mn. Potter and Rossman also conclude⁶ that either wind or water is a probable transport mechanism for the clay component of rock varnish but that water is essential in the transport of Fe and Mn. For a ferrous metal substrate only Mn would require transport and deposition, and its absence may reflect the hyperarid environment in which the artifact was recovered. It may be that the rate-determining process for varnish formation on rocks is the transport and deposition of Fe- and Mn-oxides, and that the formation of a varnish-like coating on a metal surface in a relatively short period of time is the result of an immediate source of Fe-oxide and a constant supply of wind-blown clay.

Usually less than 1% organic matter is present in rock varnish and derives from incorporation of organic plant detritus from adjacent vegetation.⁸ However, distinctive C-H absorption between 2800 and 3000 cm⁻¹ and a 12.5% carbon concentration (Table I) for the coating material clearly indicate a considerable organic component. Because this geographical region is devoid of vegetation over hundreds of square miles, organic matter is undoubtedly a residue of original paint which was scoured away by wind/sand action prior to formation of the varnish-like coating (Fig. 1).

CONCLUSIONS

A distinctive coating developed on the exterior of a metal fuel can after exposure to a hyperarid environment for 40 some odd years has been examined and found to compositionally resemble certain varieties of rock desert varnish. This is a much shorter time than usually considered necessary for the formation of varnish layers on rock surfaces. Although these studies indicate that a similar assemblage of minerals is associated with both the metal coating and orange rock varnish, development on the two types of substrate almost certainly occurs by different processes. It is unlikely that deposition of clay minerals is a rate-determining step for formation of either the metal coating or rock varnish, because clays are usually abundant and can be transported over long distances by both wind and water. However, transport, concentra-

TABLE I. Chemical composition.

Oxide	Metal coating		Orange rock varnishes	
	Fe-rich zone	Clay-rich zone	Salt Spring	Stoddard Wells
Oxide weight percents ^a				
SiO ₂	4.6	49.7	53.1	53.7
Al ₂ O ₃	2.9	18.0	27.1	26.4
Fe ₂ O ₃	85.4	21.0	8.9 ^b	10.5 ^b
Na ₂ O	1.1	0.6	0.2	0.3
MgO	0.6	2.1	4.3	3.3
K ₂ O	0.2	0.7	3.6	2.9
CaO	0.3	4.1	1.0	1.0
MnO	0.2	0.0	0.1	0.1
Cl	1.4	0.1	—	—
SO ₄	3.1	3.3	—	—
Total ^c	99.8	99.6		
H ₂ O + organics		29.3% ^d		
Mineral matter		70.7% ^e		
C = 12.5% H = 2.7% N = 0.51% ^f				

^a All analyses for metal coating except C, H, N and weight loss on ignition were by SEM/EDXRF.

^b Reported as FeO by Potter and Rossman.⁶

^c Normalized to 100% on a volatile free basis.

^d Determined by weight loss on ignition at 1000°C.

^e By difference from L.O.I.

^f CHN analyzer.

tion, and deposition of Fe- and Mn-oxides onto rock surfaces in arid regions can be very slow and erratic, because water is required for the process, and Fe and Mn are only minor constituents in rock and soil. On the other hand, the Fe-rich, Mn-poor coating on the fuel can could reasonably be expected to develop in a relatively short time as a result of an immediate and abundant source of Fe. The clays were probably transported to the metal surface by wind, which is the dominant agent of transport for sedimentary materials in this region. Surface moisture is virtually nonexistent, but even if ground surface water were present, it would not travel very far up the surface of a metal object protruding from the terrain.

It is interesting to speculate about what course the coating might take if the artifact were to survive for a few hundred years in the environment in which it was recovered. Although the Mn concentration of the clay-rich zone was nominally zero, a small concentration of the element was found in the Fe-rich zone (Table I). Mn may have existed as an additive in the substrate metal introduced during fabrication. However, this was not determined. It seems reasonable to assume that with a potential supply of Mn, either from the substrate or from external sources, a coating similar to the darker Mn-containing forms of desert varnish could be produced on the artifact over long periods of time.

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